Connections between High-Density Scaling Limits of DFT Correlation Energies and Second-Order Z^{-1} Quantum Chemistry Correlation Energy

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In the continuing search for ever-better approximations to the full density-functional correlation energy functional $E_c[n]$, we established the link between the second-order component of the correlation energy, $E_c^{(2)}[n]$ [which occurs through uniform scaling, $E_c^{(2)}[n] = \lim_{\lambda\to\infty} E_c[n_\lambda]$, where $n_\lambda(x,y,z) = \lambda^3 n(\lambda x,\lambda y,\lambda z)$], and the *known* result for the second-order Z^{-1} quantum chemistry correlation energy, $E_c^{QC,(2)}$. Except when certain degeneracies occur, $E_c^{(2)}[n] \le E_c^{QC,(2)}$, with an equality *only* for two electrons. On the other hand, the correlation energy functional ${}^{HF}E_c[n]$, whose functional derivative is meant to be added to the Hartree-Fock non-local effective potential to produce, via self-consistency, the *exact* ground-state density and ground-state energy, satisfies the *equality* ${}^{HF}E_c^{(2)}[n] = E_c^{QC,(2)}$, where ${}^{HF}E_c^{(2)}[n] = \lim_{\lambda\to\infty} {}^{HF}E_c[n_\lambda]$, for any number of electrons, except when some degeneracies occur. Because quantities $2E_c^{(2)}[n]$ and $2\,{}^{HF}E_c^{(2)}[n]$ are the initial slopes in the adiabatic connection formulas for $E_c[n]$ and ${}^{HF}E_c[n]$, respectively, the presented *equalities* involving ${}^{HF}E_c^{(2)}[n]$ are especially significant. Five numerical tests are presented for closed- and open-shell densities obtained from hydrogenic orbitals. These tests are applied to widely used approximations to correlation energies.

I. Introduction

To arrive at the very best approximations to the exact density-functional correlation energies, one needs knowledge of as many conditions as possible that reflect their properties. The idea is to modify approximate functionals so they satisfy newly discovered conditions. With this in mind, the study in this paper was undertaken.

We shall first consider the correlation energy functional $E_c[n]$. This functional[1−5] is meant to be employed as part of the full exchange-correlation functional, $E_{xc}[n]$, for variational calculations. Although $E_x[n]$ possesses simple dimensionality in that it scales homogeneously as $E_x[n_\lambda] = \lambda E_x[n]$, where $n_\lambda(x,y,z) = \lambda^3 n(\lambda x,\lambda y,\lambda z)$, $E_c[n]$ is the part of $E_{xc}[n]$ that contains the complicated dimensionality in that its scaling is not homogeneous.[5] One of the reasons that $E_c[n]$ is used instead of the traditional quantum chemistry (QC) correlation energy, E_c^{QC}, for the correlation part of $E_{xc}[n]$ is that the simple scaling for the exchange only occurs with $E_c[n]$. Thus, accurate approximations for the exchange component of $E_{xc}[n]$ are more easily obtained with the use of $E_c[n]$ than with the use of E_c^{QC}.

The simple homogeneous scaling for $E_x[n]$ stems from the fact that $E_x[n]$ is defined through the wavefunction that minimizes *only* the kinetic energy operator and yields density $n(\mathbf{r})$.[5] The scaled wavefunction, which yields the scaled density $n_\lambda(\mathbf{r})$, *also* minimizes the kinetic energy operator. The Hartree-Fock (HF) exchange energy is defined through the single determinant that minimizes the Hamiltonian for the system of interest, and yields the HF density. The scaled version of the HF wavefunction does yield the scaled HF density but does *not* minimize the same interacting Hamiltonian.[5]

There are very few known values of $E_c[n]$ for use for comparisons with approximations to $E_c[n]$. Examples include the recent two-electron results of Umrigar and Gonze.[6,7] On the other hand, we do know a number of exact values for the traditional QC correlation energy, E_c^{QC} (see, for instance, the results of Ivanova and Safronova[8] and Davidson and co-workers[9A,9B]). Consequently, in this paper we shall utilize a few of these known values of this latter familiar correlation energy. Specifically, our main goal is to establish a link between the *known* numbers obtained by means of the asymptotic $1/Z$ expansion and the previously *unknown* density functional theory (DFT) correlation energies, $E_c[n]$, of hydrogen-like densities. We introduce relationships that connect *known* results for the second-order QC correlation energy, $E_c^{QC,(2)}$, in the well-studied $1/Z$ expansion as $Z\to\infty$,[8−12] and the second-order component of the DFT correlation energy, $E_c^{(2)}[n]$, which is a result of uniform scaling of the density (i.e., $\lim_{\lambda\to\infty} E_c[n_\lambda] = E_c^{(2)}[n]$).[13−16] Previous DFT−$Z^{-1}$ connections have been made by Perdew, McMullen, and Zunger[17] and by Chakravorty and Davidson.[9A] Here the n densities shall be ground-state densities of atomic Hamiltonians without the electron−electron repulsion operator. For all nondegenerate cases, and for certain degenerate cases, we shall show that $E_c^{(2)}[n] \le E_c^{QC,(2)}$, with an equality for, and only for, two electrons.

There is an important definition for a correlation energy for which an *equality* actually generally occurs. In particular, we shall show that ${}^{HF}E_c^{(2)}[n]$ equals $E_c^{QC,(2)}$ for any number of electrons, where ${}^{HF}E_c[n]$ is defined slightly differently from $E_c[n]$, and $\lim_{\lambda\to\infty} {}^{HF}E_c[n_\lambda] = {}^{HF}E_c^{(2)}[n]$. The functional derivative of ${}^{HF}E_c[n]$ is meant to be added to the HF nonlocal potential leading to HF-like equations. The resultant modified HF equations allow one, in principle, via self-consistency, to calculate the *exact* ground-state density and the *exact* ground-state energy. For a detailed discussion of ${}^{HF}E_c[n]$, see ref 14.

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As we shall discuss, ${}^{\mathrm{HF}}E_{\mathrm{c}}^{(2)}[n]$ is especially significant because $2\,{}^{\mathrm{HF}}E_{\mathrm{c}}^{(2)}[n]$ is the initial slope in the adiabatic connection formula for ${}^{\mathrm{HF}}E_{\mathrm{c}}[n]$.

II. Definitions, Notation, and Theoretical Results

In atomic units, let us define the Hamiltonian operator $\hat{H}_\alpha$ as

$$\hat{H}_\alpha = \hat{T} + \alpha\hat{V}_{\mathrm{ee}} + \sum_{i=1}^{N} v_{\mathrm{o}}(\mathbf{r}_i) \tag{1}$$

with $\hat{T}$ being the kinetic energy operator

$$\hat{T} = \sum_{i=1}^{N} -\frac{1}{2}\nabla_i^2 \tag{2}$$

$\hat{V}_{\mathrm{ee}}$ is the operator of the electron−electron repulsion

$$\hat{V}_{\mathrm{ee}} = \sum_{i=1}^{N-1}\sum_{j=1+i}^{N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{3}$$

and $v_{\mathrm{o}}(\mathbf{r})$ is a local spin-independent multiplicative operator. (Later we shall utilize numbers for which $v_{\mathrm{o}}(\mathbf{r}) = -1/\mathbf{r}$.)

The ground-state energy of $\hat{H}_\alpha$, E_α^{GS}, is given by

$$E_\alpha^{\mathrm{GS}} = \langle \Psi_\alpha^{\mathrm{GS}} | \hat{H}_\alpha | \Psi_\alpha^{\mathrm{GS}} \rangle \tag{4}$$

where $\Psi_\alpha^{\mathrm{GS}}$ is the ground-state wavefunction of $\hat{H}_\alpha$. The HF energy E_α^{HF} is defined as

$$E_\alpha^{\mathrm{HF}} = \langle \Phi_\alpha^{\mathrm{HF}} | \hat{H}_\alpha | \Phi_\alpha^{\mathrm{HF}} \rangle \tag{5}$$

where $\Phi_\alpha^{\mathrm{HF}}$ is the single determinant that minimizes $\langle \hat{H}_\alpha \rangle$.

The QC correlation energy $E_{\mathrm{c},\alpha}^{\mathrm{QC}}$ is defined as the difference between E_α^{GS} and E_α^{HF};[10,13] namely,

$$E_{c,\alpha}^{\mathrm{QC}} \equiv E_\alpha^{\mathrm{GS}} - E_\alpha^{\mathrm{HF}} = \langle \Psi_\alpha^{\mathrm{GS}} | \hat{H}_\alpha | \Psi_\alpha^{\mathrm{GS}} \rangle - \langle \Phi_\alpha^{\mathrm{HF}} | \hat{H}_\alpha | \Phi_\alpha^{\mathrm{HF}} \rangle \tag{6}$$

We first follow Linderberg and Shull[11] and discuss the perturbation expansion for $E_{\mathrm{c},\alpha}^{\mathrm{QC}}$, for small enough α. By applying the standard Rayleigh-Schrödinger perturbation theory, we develop expansions for E_α^{GS} and E_α^{HF} and their respective wavefunctions $\Psi_\alpha^{\mathrm{GS}}$ and $\Phi_\alpha^{\mathrm{HF}}$. The energy expressions read as follows:

$$E_\alpha^{\mathrm{GS}} = E_{\mathrm{o}} + \alpha^1 E_{\mathrm{GS}}^{(1)} + \alpha^2 E_{\mathrm{GS}}^{(2)} + \alpha^3 E_{\mathrm{GS}}^{(3)} \ldots = E_{\mathrm{o}} + \sum_{j=1}^{\infty} \alpha^j E_{\mathrm{GS}}^{(j)} \tag{7}$$

$$E_\alpha^{\mathrm{HF}} = E_{\mathrm{o}} + \alpha^1 E_{\mathrm{HF}}^{(1)} + \alpha^2 E_{\mathrm{HF}}^{(2)} + \alpha^3 E_{\mathrm{HF}}^{(3)} \ldots = E_{\mathrm{o}} + \sum_{j=1}^{\infty} \alpha^j E_{\mathrm{HF}}^{(j)} \tag{8}$$

In eqs 7 and 8, E_{o} is the ground-state energy of $\hat{H}_{\mathrm{o}}$ (i.e., $\hat{H}_\alpha$ at $\alpha = 0$). The eigenvalue problem corresponding to $\hat{H}_{\mathrm{o}}$ is

$$\hat{H}_{\mathrm{o}}\Phi_k = E_k\Phi_k \qquad E_{\mathrm{o}} < E_1 \le E_2 \le \ldots \le E_k \le \ldots \tag{9}$$

where we shall concern ourselves with situations where E_{o} is nondegenerate. (Note that $\hat{H}_{\mathrm{o}}$ is a Kohn-Sham Hamiltonian and that Φ_{o} is a Kohn-Sham determinant.) For $k > 0$, Φ_k are the excited-state wavefunctions of $\hat{H}_{\mathrm{o}}$.

The corresponding series for the wavefunctions $\Psi_\alpha^{\mathrm{GS}}$ and $\Phi_\alpha^{\mathrm{HF}}$ are

$$\Psi_\alpha^{\mathrm{GS}} = \Psi_{\mathrm{GS}}^{(0)} + \alpha^1\Psi_{\mathrm{GS}}^{(1)} + \alpha^2\Psi_{\mathrm{GS}}^{(2)} + \alpha^3\Psi_{\mathrm{GS}}^{(3)} \ldots = \sum_{j=0}^{\infty} \alpha^j \Psi_{\mathrm{GS}}^{(j)} \tag{10}$$

and

$$\Phi_\alpha^{\mathrm{HF}} = \Phi_{\mathrm{HF}}^{(0)} + \alpha^1\Phi_{\mathrm{HF}}^{(1)} + \alpha^2\Phi_{\mathrm{HF}}^{(2)} + \alpha^3\Phi_{\mathrm{HF}}^{(3)} \ldots = \sum_{j=0}^{\infty} \alpha^j \Phi_{\mathrm{HF}}^{(j)} \tag{11}$$

When $\hat{H}_{\mathrm{o}}$ has a nondegenerate ground state, both series begin with the same Φ_{o}, which is the ground-state solution to eq 9, $k = 0$. In other words, $\Psi_{\mathrm{GS}}^{(0)} = \Phi_{\mathrm{HF}}^{(0)} = \Phi_{\mathrm{o}}$. Unless otherwise stated, this nondegeneracy shall be assumed.

The second and third terms in the corresponding expansions for E_α^{GS} and E_α^{HF}, with nondegenerate E_{o}, are

$$E_{\mathrm{GS}}^{(1)} = E_{\mathrm{HF}}^{(1)} = \langle \Phi_{\mathrm{o}} | \hat{V}_{\mathrm{ee}} | \Phi_{\mathrm{o}} \rangle \tag{12}$$

$$E_{\mathrm{GS}}^{(2)} = \frac{1}{2}\langle \Phi_{\mathrm{o}} | \hat{V}_{\mathrm{ee}} | \Psi_{\mathrm{GS}}^{(1)} \rangle + \frac{1}{2}\langle \Psi_{\mathrm{GS}}^{(1)} | \hat{V}_{\mathrm{ee}} | \Phi_{\mathrm{o}} \rangle \tag{13}$$

and

$$E_{\mathrm{HF}}^{(2)} = \frac{1}{2}\langle \Phi_{\mathrm{o}} | \hat{V}_{\mathrm{ee}} | \Phi_{\mathrm{HF}}^{(1)} \rangle + \frac{1}{2}\langle \Phi_{\mathrm{HF}}^{(1)} | \hat{V}_{\mathrm{ee}} | \Phi_{\mathrm{o}} \rangle \tag{14}$$

To preserve the general character of eqs 13 and 14, the explicit complex forms of the wavefunctions are kept, even though the energies are real. By subtracting eq 8 from eq 7, along with making use of eqs 12−14, one obtains[11] an expression for $E_{\mathrm{c},\alpha}^{\mathrm{QC}}$ that begins with $\alpha^2 E_{\mathrm{c}}^{\mathrm{QC},(2)}$:

$$E_{\mathrm{c},\alpha}^{\mathrm{QC}} = \alpha^2 E_{\mathrm{c}}^{\mathrm{QC},(2)} + \alpha^3 E_{\mathrm{c}}^{\mathrm{QC},(3)} \ldots = \sum_{j=2}^{\infty} \alpha^i E_{\mathrm{c}}^{\mathrm{QC},(j)} \tag{15}$$

with

$$E_{\mathrm{c}}^{\mathrm{QC},(j)} \equiv E_{\mathrm{GS}}^{(j)} - E_{\mathrm{HF}}^{(j)} \tag{16}$$

When the ground state of $\hat{H}_{\mathrm{o}}$ is degenerate, the expansion for $E_{\mathrm{c},\alpha}^{\mathrm{QC}}$ is expected, in general, to begin[11] with term linear in α because $E_{\mathrm{GS}}^{(1)} < E_{\mathrm{HF}}^{(1)}$.

The second-order energy $E_{\mathrm{c}}^{\mathrm{QC},(2)}$, given in terms of eigenstates of $\hat{H}_{\mathrm{o}}$, reads

$$E_{\mathrm{c}}^{\mathrm{QC},(2)} = \sum_{\substack{k=1\\ -\\ \mathrm{DE}}}^{\infty} \frac{|\langle \Phi_k | \hat{V}_{\mathrm{ee}} | \Phi_{\mathrm{o}} \rangle|^2}{E_{\mathrm{o}} - E_k} \tag{17}$$

In eq 17, DE signifies double excitations. In other words, the summation in eq 17 goes over those eigenstates Φ_k of $\hat{H}_{\mathrm{o}}$ that are obtained by exciting two electrons from Φ_{o}. There is no contribution coming from singly excited states (see the Appendix).

Next, we turn our attention to the correlation energy $E_{\mathrm{c}}[n]$ defined by

$$E_{\mathrm{c}}[n] \equiv \langle \Psi_n | \hat{T} + \hat{V}_{\mathrm{ee}} | \Psi_n \rangle - \langle \Phi_n^{\mathrm{KS}} | \hat{T} + \hat{V}_{\mathrm{ee}} | \Phi_n^{\mathrm{KS}} \rangle \tag{18}$$

According to the constrained-search formulation of DFT[2], Ψ_n is, among all wavefunctions that yield the density $n(\mathbf{r})$, the one that minimizes the expectation value $\langle \hat{T} + \hat{V}_{ee} \rangle$. Similarly, Φ_n^{KS}, the Kohn-Sham (KS) wavefunction, is among all wavefunctions yielding $n(\mathbf{r})$, the one that minimizes just $\langle \hat{T} \rangle$ (i.e., the wavefunction with the lowest kinetic energy). $E_c[n]$ is meant to be used in a *full* traditional density functional calculation. (Note that $\Phi_o = \Phi_n^{KS}$.)

The correlation energy functional ${}^{HF}E_c[n]$ is defined by

$$ {}^{HF}E_c[n] \equiv \langle \Psi_n | \hat{T} + \hat{V}_{ee} | \Psi_n \rangle - \langle \Phi_n^{HF} | \hat{T} + \hat{V}_{ee} | \Phi_n^{HF} \rangle \quad (19) $$

where Φ_n^{HF} is the single determinant that minimizes the expectation value $\langle \hat{T} + \hat{V}_{ee} \rangle$ and yields the density $n(\mathbf{r})$. The functional derivative of ${}^{HF}E_c[n]$ is meant to be added to the HF nonlocal potential to produce HF-like equations, whose solution upon self-consistency, in principle, leads to the *exact* density and to the *exact* ground-state energy.[14] Without this added functional derivative, the familiar HF density and energy are obtained upon self-consistency. Note that ${}^{HF}E_c[n]$ is *different* from traditional QC correlation energy. In the HF theory, one is interested in the single determinant that minimizes the Hamiltonian of the system under investigation without any constraints on the density. According to eq 19, Φ_n^{HF} can be viewed as the single determinant that minimizes the same Hamiltonian but yields the *ground-state* density.

We shall derive relationships between the leading second-order components for $E_c[n]$ and ${}^{HF}E_c[n]$ and the second-order energy $E_c^{QC,(2)}$, because published numbers are *already available* for the latter, and we shall present these numbers. Here $n(\mathbf{r})$ is density of Φ_o; namely, we shall derive

$$ \lim_{\lambda \to \infty} E_c[n_\lambda] \equiv E_c^{(2)}[n] \le E_c^{QC,(2)} \quad (20A) $$

with an equality for only the two-electron case. And, we shall also derive

$$ \lim_{\lambda \to \infty} {}^{HF}E_c[n_\lambda] \equiv {}^{HF}E_c^{(2)}[n] = E_c^{QC,(2)} \quad (20B) $$

The latter equality holds for any number of electrons, with the caveat of nondegeneracy for Φ_o. The uniformly scaled density $n_\lambda(\mathbf{r})$ in eq 20 is given by

$$ n_\lambda(\mathbf{r}) = \lambda^3\, n(\lambda \mathbf{r}) = \lambda^3\, n(\lambda x, \lambda y, \lambda z) \quad (21) $$

where $n(\mathbf{r})$ is the ground-state density of the Kohn-Sham $\hat{H}_o$ in eq 9.

The adiabatic connection formula for ${}^{HF}E_c[n]$ given by Stoll and Savin is[18]

$$ {}^{HF}E_c[n] = \int_0^1 {}^{HF}V_c^{\alpha}[n]\, d\alpha \quad (22) $$

where

$$ {}^{HF}V_c^{\alpha}[n] = \langle \Psi_n^{\min,\alpha} | \hat{V}_{ee} | \Psi_n^{\min,\alpha} \rangle - \langle \Phi_n^{HF,\alpha} | \hat{V}_{ee} | \Phi_n^{HF,\alpha} \rangle \quad (23) $$

where $\Psi_n^{\min,\alpha}$ is the wavefunction that minimizes $\langle \hat{T} + \alpha \hat{V}_{ee} \rangle$ and yields $n(\mathbf{r})$, and where $\Phi_n^{HF,\alpha}$ is the single determinant that minimizes $\langle \hat{T} + \alpha \hat{V}_{ee} \rangle$ and yields the same density $n(\mathbf{r})$. Approximations to ${}^{HF}V_c^{\alpha}[n]$ have stimulated the development of successful hybrid schemes for approximating ${}^{HF}E_c[n]$ (see ref 19 and references within).

For small enough coupling constant α, it has been shown that[14]

$$ {}^{HF}V_c^{\alpha}[n] = 2\alpha\, {}^{HF}E_c^{(2)}[n] \quad (24) $$

Hence, for arbitrary $n(\mathbf{r})$, the quantity $2\,{}^{HF}E_c^{(2)}[n]$ is especially important because it is the initial slope (slope at zero α) of the integrand ${}^{HF}V_c^{\alpha}[n]$ for the correlation energy, ${}^{HF}E_c[n]$, in eq 22. Further, when approximating ${}^{HF}V_c^{\alpha}[n]$ for use in eq 22, we can approximate ${}^{HF}E_c^{(2)}[n]$ by approximating $\lim_{\lambda \to \infty} {}^{HF}E_c[n_\lambda]$; so it is important to know the exact values for the latter limit, as reported in this paper.

III. Numerical Results

The Hamiltonian given by eq 1, for the special test case when $v_o(\mathbf{r}) = -1/\mathbf{r}$, is the same as the one that appears in the well-known $1/Z$ expansion of the QC correlation energy. Consequently, we are able to use known second-order results, $E_c^{QC,(2)}$, to test approximations to the DFT correlation energies $E_c[n]$ and ${}^{HF}E_c[n]$. We shall consider numbers for $E_c^{QC,(2)}$ associated with HF energies resulting from restricted HF calculations. In other words, the calculation of $E_c^{QC,(2)}$ corresponding to

$$ \hat{H}_\alpha = \hat{T}(\mathbf{r}_1,...,\mathbf{r}_N) + \alpha \hat{V}_{ee}(\mathbf{r}_1,...,\mathbf{r}_N) - \sum_{i=1}^{N} \frac{1}{\mathbf{r}_i} \qquad \alpha = Z^{-1} \quad (25) $$

as well as higher-order energy terms has been of interest for quite a long time,[8−12] and there are many available numbers of very high accuracy, mainly by Ivanova and Safronova[8] and recently by Davidson and co-workers.[9A,9B]

To test approximations of $E_c[n_\lambda]$ and ${}^{HF}E_c[n_\lambda]$, as $\lambda \to \infty$, we take the exact values for the second-order energy $E_c^{QC,(2)}$ associated with eq 25, for five different hydrogenic densities.[8,9A] The two- and 10-electron densities are generated from the nondegenerate ground-state wavefunctions of the noninteracting $\hat{H}_o$ in eq 25. For the three-, nine-, and 11-electron densities, the ground state of $\hat{H}_o$ in eq 25 is degenerate, but the expansion for $E_{c,\alpha}^{QC}$ still begins with $E_c^{QC,(2)}$ because of symmetry, according to Linderberg and Schull.[11] The three-, nine-, and 11-electron densities are obtained from Φ_o wavefunctions that correspond to configurations $1s^2 2s$, $1s^2 2s^2 2p^5$, and $1s^2 2s^2 2p^6$-$3s$, respectively.

We compare, in Table 1, the values of $E_c^{QC,(2)}$ with those of $E_c^{APP}[n_\lambda]$, as $\lambda \to \infty$, where $E_c^{APP}[n_\lambda]$ refers to three approximate correlation energy functionals with gradients; that is, the recently derived GGA of Perdew, Burke, and Ernzerhof (PBE),[20] the one of Lee, Yang, and Parr (LYP),[21] and the one of Levy and Wilson.[22]

The second column in the table is the value corresponding to $\lim_{\lambda \to \infty} {}^{HF}E_c[n_\lambda] = E_c^{QC,(2)}$ when $n(\mathbf{r})$ is the hydrogenic ground-state density of $\hat{H}_o$ in eq 25. For $E_c[n]$, as required by eq 20A for more than two electrons, the tested approximations give more negative values than the respective values for $E_c^{QC,(2)}$. For a two-electron density, the equality $E_c^{(2)}[n] = {}^{HF}E_c^{(2)}[n] = E_c^{QC,(2)}$ is desired.

The functionals give reasonable to good values, depending on the functional and the number of electrons. When the adiabatic connection formula (eq 22) is employed to generate a new approximation to ${}^{HF}E_c[n]$, there is room for improvement with all three functionals when these functionals are used to approximate the $2E_c^{QC,(2)}$ segment of the integrand, which is the initial slope in this adiabatic connection formula.

TABLE 1: Comparison of $E_c^{QC,(2)}$ for $\hat{H}_\alpha^{QC}$ in Equation 25 with $E_c^{APP}[n_\lambda]$[a]

density	$E_c^{QC,(2)}$	$\lim_{\lambda\to\infty} E_c^{PBE}[n_\lambda]$	$\lim_{\lambda\to\infty} E_c^{LYP}[n_\lambda]$	$\lim_{\lambda\to\infty} E_c^{WL}[n_\lambda]$
2-electron	−0.0467[b]	−0.0479	−0.0565	−0.0480
3-electron	−0.0537[c]	−0.0584	−0.0991	−0.0568
9-electron	−0.3694[c]	−0.3856	−0.4648	−0.3826
10-electron	−0.4278[c]	−0.4577	−0.5275	−0.4504
11-electron	−0.4534[d]	−0.4753	−0.5868	−0.4718

[a] Determined as $\lambda \to \infty$, where n is the ground-state density of $\hat{H}_o^{QC}$. [b] From refs 8, 9A, and 16. [c] From ref 8. [d] From ref 9A.

IV. Derivations of Equations 20A and 20B

Görling and Levy[14] have recently introduced an adiabatic DFT perturbation theory. The effective potential and the electron−electron interaction along the coupling constant path, which connects a noninteracting and a fully interacting system with the *same* electron density, have been used for this DFT perturbation theory.[14,15] By using their perturbation theory, they have derived the following high-λ expansion for $E_c[n]$:

$$E_c[n_\lambda] = E_c^{(2)}[n] + \lambda^{-1}E_c^{(3)}[n] + \lambda^{-2}E_c^{(4)}[n] + ... \quad (26)$$

and they have identified the second-order energy $E_c^{(2)}[n]$ as

$$\lim_{\lambda\to\infty} E_c[n_\lambda] = E_c^{(2)}[n] = \sum_{k=1}^{\infty} \frac{|\langle \Phi_k|\Delta\hat{V}|\Phi_o\rangle|^2}{E_o - E_k} \quad (27)$$

with

$$\Delta\hat{V} = \hat{V}_{ee} - \sum_{i=1}^{N}\{u([n];\mathbf{r}_i) + v_x([n];\mathbf{r}_i)\} \quad (28)$$

and where

$$u([n];\mathbf{r}_i) = \int \frac{n(\mathbf{r}_i)}{|\mathbf{r}_i - \mathbf{r}|}\, dr \quad (29)$$

In eq 28, the Hartree potential $u([n];\mathbf{r})$ and the exchange potential $v_x([n];\mathbf{r})$ are local multiplicative potentials obtained by taking functional derivatives of $U[n]$ and $E_x[n]$ with respect to the density $n(\mathbf{r})$. The density $n(\mathbf{r})$ is obtained from the noninteracting Φ_o, the Kohn-Sham single determinant. The Hartree electron−electron repulsion energy $U[n]$ and the exchange energy $E_x[n]$ are defined as follows:

$$U[n] = \frac{1}{2}\int\int \frac{n(\mathbf{r}_1)n(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}\, d\mathbf{r}_1 d\mathbf{r}_2 \quad (30)$$

$$E_x = \langle \Phi_o|\hat{V}_{ee}|\Phi_o\rangle - U[n] \quad (31)$$

By utilizing the fact that $\hat{V}_{ee}$ is a two-body operator, and $u([n];\mathbf{r})$ and $v_x([n];\mathbf{r})$ are one-body operators, we separate the infinite summation in eq 27 in two parts: summation over single excitations and summation over double excitations. For simplicity of the notation, we define $v_{xu}([n];\mathbf{r}) = u([n];\mathbf{r}) + v_x([n];\mathbf{r})$. As a result, eq 27 is re-expressed as

$$E_c^{(2)}[n] = \sum_{\substack{k=1\\ -\\ \mathrm{SE}}}^{\infty} \frac{|\langle \Phi_k|\Delta\hat{V}|\Phi_o\rangle|^2}{E_o - E_k} + \sum_{\substack{k=1\\ -\\ \mathrm{DE}}}^{\infty} \frac{|\langle \Phi_k|\hat{V}_{ee}|\Phi_o\rangle|^2}{E_o - E_k} \quad (32)$$

By making use of eq 17, we obtain

$$E_c^{(2)}[n] = E_c^{QC,(2)} + \sum_{\substack{k=1\\ -\\ \mathrm{SE}}}^{\infty} \frac{|\langle \Phi_k|\hat{V}_{ee} - \sum_{i=1}^{N} v_{xu}([n];\mathbf{r}_i)|\Phi_o\rangle|^2}{E_o - E_k} \quad (33)$$

Because of the nonpositive contributions from all single excitations in eq 33, it follows that

$$E_c^{(2)}[n] \le E_c^{QC,(2)} \quad (34)$$

with an *equality* only for two-electron systems, because only for two electrons does each term vanish in the summation over single excitations in eq 33.

For the high-density scaling limit of ${}^{HF}E_c[n]$, Görling and Levy[14] arrived at

$${}^{HF}E_c[n_\lambda] = {}^{HF}E_c^{(2)}[n] + \lambda^{-1}\, {}^{HF}E_c^{(3)}[n] + \lambda^{-2}\, {}^{HF}Ec^{(4)}[n] + ... \quad (35)$$

with

$$\lim_{\lambda\to\infty} {}^{HF}E_c[n_\lambda] = {}^{HF}E_c^{(2)}[n] = \sum_{k=1}^{\infty} \frac{|\langle \Phi_k|\hat{V}_{ee} - \sum_{i=1}^{N}\{\hat{v}_x^{HF}([\Phi_o];\mathbf{r}_i) + u([n];\mathbf{r}_i)\}|\Phi_o\rangle|^2}{E_o - E_k} \quad (36)$$

In the eq 36 formula, $\hat{v}_x^{HF}([\Phi_o];\mathbf{r})$ is the familiar nonlocal Fock exchange operator, but here built from the one-particle orbitals of Φ_o instead of from the HF orbitals. By applying identity (eq A9) to eq 36 and invoking eq 17, we express ${}^{HF}E_c^{(2)}[n]$ as

$${}^{HF}E_c^{(2)}[n] = \sum_{\substack{k=1\\ -\\ \mathrm{DE}}}^{\infty} \frac{|\langle \Phi_k|\hat{V}_{ee}|\Phi_o\rangle|^2}{E_o - E_k} = E_c^{QC,(2)} \quad (37)$$

The combination of eqs 33, 34, and 37 leads to eqs 20A and 20B.

V. Concluding Comments

We have established the link between the second-order component of the *unknown* DFT correlation energy, $E_c^{(2)}[n]$, and the *known* result for the second-order quantum chemistry correlation energy, $E_c^{QC,(2)}$. We have also shown that, except for the existence of certain degeneracies, the leading second-order term in the high-density expansion for the correlation energy functional ${}^{HF}E_c[n]$ satisfies the *equality* ${}^{HF}E_c^{(2)}[n] = E_c^{QC,(2)}$. The quantity 2 ${}^{HF}E_c^{(2)}[n]$ is especially important because it is the initial slope of the adiabatic connection formula for the correlation energy ${}^{HF}E_c[n]$, for all densities, not just for those in the high-density limit. The functional derivative of ${}^{HF}E_c[n]$ is meant to be added to the HF nonlocal effective potential to produce, via self-consistency, the exact ground-state density and ground-state energy. Five numerical tests on viable approximations were presented for closed- and open-shell densities obtained from hydrogenic orbitals. These tests should be used to assess approximations to correlation energies. Moreover, it is possible to generate data for different sets of densities if one uses the corresponding $v_o(\mathbf{r})$ for which the eigenfunctions and eigenvalues, corresponding to $\hat{H}_o$ with this

$v_o(\mathbf{r})$, are determined. For example, if $v_o(\mathbf{r}) = \mathbf{r}^2$, then one has the Harmonium (Hooke's) Atom.[23–25]

Recently, Huang and Umrigar[25] have numerically studied the Z^{-1} expansion for the DFT correlation energy for two-electron densities and found that the respective series begins with the same second-order energy as the similar Z^{-1} expansion for traditional QC correlation energy. A formal proof of their observation as well as a generalization to more than two electrons have very recently been derived by Ivanov and Levy.[26]

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Appendix

In this section we will present a derivation of eq 17. By subtracting eq 14 from eq 13, one obtains an expression for $E_c^{QC,(2)}$ in terms of $\Psi_{GS}^{(1)}$and $\Phi_{HF}^{(1)}$:

$$E_c^{QC,(2)} = \frac{1}{2}\langle\Phi_o|\hat{V}_{ee}|\{\Psi_{GS}^{(1)} - \Phi_{HF}^{(1)}\}\rangle + \frac{1}{2}\langle\{\Psi_{GS}^{(1)} - \Phi_{HF}^{(1)}\}|\hat{V}_{ee}|\Phi_o\rangle \tag{A1}$$

where $\Psi_{GS}^{(1)}$ is expanded in the usual way

$$\Psi_{GS}^{(1)} = \sum_{k=1}^{\infty}\frac{\langle\Phi_k|\hat{V}_{ee}|\Phi_o\rangle}{E_o - E_k}\Phi_k \tag{A2}$$

To find $\Phi_{HF}^{(1)}$, we shall consider the equation to which Φ_α^{HF} is an eigenfunction. From HF theory it is known that for every α, Φ_α^{HF} is solution to

$$\{\hat{T} + \alpha\sum_{i=1}^{N}\hat{v}^{HF}([\Phi_\alpha^{HF}];\mathbf{r}_i) + \sum_{i=1}^{N}v_o(\mathbf{r}_i)\}\Phi_\alpha^{HF} = \bar{E}_\alpha^{HF}\Phi_\alpha^{HF} \tag{A3}$$

Note that $\bar{E}_\alpha^{HF}$ is different from E_α^{HF} in that the former is the sum of HF orbital energies. The potential $v_o(\mathbf{r})$ in eq A3 is a local multiplicative one. With $v_o(\mathbf{r}) = -Z/\mathbf{r}$ and $\alpha = 1$, eq A3 leads to the familiar HF equations. In formula A3, $\hat{v}^{HF}([\Phi_\alpha^{HF}];\mathbf{r})$ is the HF nonlocal effective potential that has two contributions: the nonlocal exchange potential $\hat{v}_x^{HF}([\Phi_\alpha^{HF}];\mathbf{r})$ built from the occupied one-particle orbitals of Φ_α^{HF}, and the local Hartree potential $u([n_\alpha^{HF}];\mathbf{r}]$, associated with the density $n_\alpha^{HF}(\mathbf{r})$ obtained from Φ_α^{HF}:

$$\hat{v}^{HF}([\Phi_\alpha^{HF}];\mathbf{r}_i) = \hat{v}_x^{HF}([\Phi_\alpha^{HF}];\mathbf{r}_i) + u([n_\alpha^{HF}];\mathbf{r}_i) \tag{A4}$$

For small enough α, $\bar{E}_\alpha^{HF}$ is expanded in the following way

$$\bar{E}_\alpha^{HF} = E_o + \alpha^1\bar{E}_{HF}^{(1)} + \alpha^2\bar{E}_{HF}^{(2)} + \alpha^3\bar{E}_{HF}^{(3)} ... = E_o + \sum_{j=1}^{\infty}\alpha^j\bar{E}_{HF}^{(j)} \tag{A5}$$

Upon substituting eqs 11 and A5 in eq A3 and by equating all terms of order one, we obtain

$$[\hat{H}_o - E_o]\Phi_{HF}^{(1)} = [\bar{E}_{HF}^{(1)} - \sum_{i=1}^{N}\hat{v}_x^{HF}([\Phi_o];\mathbf{r}_i) + u([n];\mathbf{r}_i)]\Phi_o \tag{A6}$$

In terms of eigenfunctions of $\hat{H}_o$, $\Phi_{HF}^{(1)}$ is given by

$$\Phi_{HF}^{(1)} = \sum_{k=1}^{\infty}\frac{\langle\Phi_k|\sum_{i=1}^{N}\hat{v}^{HF}([\Phi_o];\mathbf{r}_i)|\Phi_o\rangle}{E_o - E_k}\Phi_k \tag{A7}$$

By subtracting eq A7 from eq A1, one finds

$$\Psi_{GS}^{(1)} - \Phi_{HF}^{(1)} = \sum_{k=1}^{\infty}\frac{\langle\Phi_k|\hat{V}_{ee} - \sum_{i=1}^{N}\hat{v}^{HF}([\Phi_o];\mathbf{r}_i)|\Phi_o\rangle}{E_o - E_k}\Phi_k = \sum_{\substack{k=1\\ -\\ \mathrm{SE}}}^{\infty}\frac{\langle\Phi_k|\hat{V}_{ee} - \sum_{i=1}^{N}\hat{v}^{HF}([\Phi_o];\mathbf{r}_i)|\Phi_o\rangle}{E_o - E_k}\Phi_k + \sum_{\substack{k=1\\ -\\ \mathrm{DE}}}^{\infty}\frac{\langle\Phi_k|\hat{V}_{ee}|\Phi_o\rangle}{E_o - E_k}\Phi_k \tag{A8}$$

Because for every k corresponding to singly-excited determinant,

$$\langle\Phi_k|\hat{V}_{ee} - \sum_{i=1}^{N}\hat{v}^{HF}([\Phi_o];\mathbf{r}_i)|\Phi_o\rangle = 0 \tag{A9}$$

the summation over all single excitations drops out and the difference $\{\Psi_{GS}^{(1)} - \Phi_{HF}^{(1)}\}$ becomes

$$\Psi_{GS}^{(1)} - \Phi_{HF}^{(1)} = \sum_{\substack{k=1\\ -\\ \mathrm{DE}}}^{\infty}\frac{\langle\Phi_k|\hat{V}_{ee}|\Phi_o\rangle}{E_o - E_k}\Phi_k \tag{A10}$$

Hence, the expression for $E_c^{QC,(2)}$ contains a summation over doubly-excited states only:

$$E_c^{QC,(2)} = \sum_{\substack{k=1\\ -\\ \mathrm{DE}}}^{\infty}\frac{|\langle\Phi_k|\hat{V}_{ee}|\Phi_o\rangle|^2}{E_o - E_k} \tag{A11}$$

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